Appendix E

APPENDIX E

PROCEDURES FOR ESTABLISHING TRACEABILITY OF GASES FOR CALIBRATING CONTINUOUS ANALYZERS

Claims of traceability established by manufacturers or vendors should not be relied upon. Calibration gases should be analyzed by analytical chemists. The chemist may elect to use either an analytical instrument such as a gas chromatograph or wet chemical methods in calibrating cylinder gases. The chemist must follow the prescribed procedures to assure the precision and accuracy of the cylinder gas analysis.

No gas cylinder is to be analyzed prior to the fifth day after filling, this is to permit the concentration to stabilize. All analyses are performed in triplicate to expose erroneous data points and excessive random variations in instrument response.

PROTOCOL FOR ANALYTICAL GAS CYLINDER ANALYSIS

1. Analyze each cylinder gas directly against the nearest standard reference material (SRM) by alternate analyses of the SRM and calibration gas in triplicate. Adjust the instrument span if necessary prior to analysis. No instrument adjustments are permitted during the triplicate analyses. The response to zero gas is frequently checked so that the change in successive zero responses do not exceed 1% of full scale.

2. For each of the six analyses, determine the apparent concentration of the SRM or cylinder gas from the calibration curve.

3. For each pair of analyses (one SRM and one cylinder gas), calculate the concentration of the cylinder gas by:

$$\text{True Conc of Cyl. Gas} = \text{Apparent Conc. of Cyl. Gas} \times \frac{\text{True Conc. of SRM}}{\text{Apparent Conc of SRM}}$$

4. Determine the mean of the three values for true concentration of the cylinder gas.

5. If any one value differs from the mean by greater than 1.5%, discard the data, reset the instrument span, if necessary, and repeat steps 1 to 4.

The following information is recorded on a label affixed to the cylinder.

1. Cylinder number

2. Mean concentration of cylinder gas, ppm or mole %

3. Replicate analysis data

4. SRM number use as primary standards

5. Analytical principle used

6. Date of analysis

A cylinder calibration analysis report including all of the data shown above is prepared. This report should be placed in the files and maintained for three years.

PROCEDURE FOR INSTRUMENT CALIBRATION

The following procedure for periodic multipoint calibration and daily instrument span checks is prescribed to minimize systematic errors. Separate procedures are used to perform span checks for linear and non-linear instruments. In this context, a linear instrument is defined as one that yields a calibration curve which deviates by 2% of full scale or less from a straight line drawn from the point determined by zero gas to the highest calibration point. To be considered linear, the difference between the concentrations indicated by the calibration curve and the straight line must not exceed 2% of full scale at any point on the curve.

INSTRUMENT SPAN CHECKS

LINEAR RESPONSE ANALYTICAL INSTRUMENT

At the start and end of each test day (or test period) during which cylinder gases are to be analyzed, check instrument response to the highest SRM in the range to be used and to zero gas. Adjust response to the value obtained in the most recent multipoint calibration. Cylinder gases analyzed with a linear instrument must not have a concentration greater than 15% above the highest available SRM concentration.

NON-LINEAR RESPONSE ANALYTICAL INSTRUMENT

At the start of each test day (or test period) during which cylinder gases are to be analyzed, check instrument response to two SRMs in the range of calibration gases to be analyzed and to zero gas as follows. First, set the instrument zero with zero gas and then adjust the instrument response to the highest SRM available or to the value obtained in the most recent multipoint calibration. Next, make one check with the SRM nearest in concentration to the expected concentration of the source. If the response to the lower standard varies by greater than 2% from the response obtained, in the most recent multipoint

calibration, a full multipoint calibration must be performed. Multipoint calibration will be discussed in detail in the next paragraph. Calibration gases analyzed with a non-linear instrument must not have a concentration greater than the highest available SRM concentration.

MULTIPOINT CALIBRATION

A multipoint calibration curve is prepared by using two SRM cylinder gases and a zero gas. The zero gas must not contain more than 0.2% of the full scale concentration of the component being analyzed. The zero gas must be free of any impurity that will give a response on the analytical instrument.

A multipoint calibration is accomplished by diluting the highest SRM with zero gas using a calibration flow system. Obtain the instrument response for points representing 0, 50, 90 and 100% of each expected range concentration curve. Obtain the instrument response for the other lower SRM without dilution. Compare the apparent concentration from the calibration of the lower SRM. If the difference between the apparent concentration and the true concentration of the lower SRM exceeds 2% of the true concentration, repeat the multipoint calibration procedure.

PROCEDURE FOR ANALYSIS OF CYLINDER GAS

The following procedure is designed to assure the precision and accuracy of cylinder gas analyses. The analyses involve the direct comparison of the cylinder gas to the SRM in order to compensate for variations in instrument response between the time of the initial span check and the time of analysis. Significant variations in instrument response often result from changes in room temperature, line voltage, etc. These variations are minimized by using air conditioned source test vans and by using the power supply available at the source during the entire testing period including the initial calibration and span checks.

Verification of Cylinder Gas Stability

The stability of reactive gases (including cylinder gas of nitric oxide and carbon monoxide) must be verified before use. The stability of cylinder gas is verified by performing a second set of triplicate analyses (using procedure described above) a minimum of 7 days after the first set of triplicate analyses. The mean of the second triplicate analyses must not differ from the mean of the first triplicate analysis by more than 1%.

Reanalysis of Cylinder Gases

All cylinder gases which are six months or longer in stock must be reanalysed before use.

Minimum Cylinder Pressure

No cylinder gas should be used below a cylinder pressure of 200 psi or 10% of its initial pressure.

Cylinder Label and Analysis Report

Each gas cylinder should contain the following minimum traceability information on a label affixed to the cylinder.

1. Cylinder number.

2. Mean concentration of cylinder gas, ppm or mole %.

3. Last recorded pressure.

4. Last analysis date.

5. Date when reanalysis is required (six months after date shown in #4).

The table below lists the required cylinder types and recommended intervals for checking span gas concentrations.

GAS	CYLINDER MATERIAL	FREQUENCY OF RE-CERTIFICATION*	MINIMUM USABLE CYLINDER PRESSURE, PSIG
SO_2	Aluminum	6 months	200
NO, NO_X	Aluminum	6 months	200
CO	Aluminum	6 months	200
HC	Aluminum[1/]	6 months	200[2/]
CO_2	Aluminum[1/]	6 months	200[2/]

* may be longer if guaranteed by manufacturer.
[1/] Steel may be used if aluminum is not available
[2/] 400 PSL with steel

Aluminum cylinders are much more effective than steel for stabilizing concentrations of SO_2, NO_X, and CO. This is partly because of the decreased cylinder surface area of the aluminum cylinders due to a much smoother surface. When aluminum cylinders are not available for SO_2, NO_X, and CO, steel containers may be used, but they should be re-certified once a month. The minimum usable cylinder pressures are shown above. This is important because changes in temperature moisture and vapor pressure produce changes in concentration as the tank pressure decreases.

Newly purchased gas standards should always be checked against old ones as a basic check of the gases themselves, the gas manufacturer, and the sampling instrument.